DEPARTMENT OF THE INTERIOR U.S. GEOLOGICAL SURVEY

Opal claystone associated with phosphate rock in northern Saudi Arabia

by

1/ W. F. Outerbridge and C. R. Meissner, Jr.

Open-File Report 86- 103

Report prepared for Ministry of Petroleum and Mineral Resources, Deputy Ministry for Mineral Resources, Saudi Arabia

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature.

1/ U.S. Geological Survey, Reston, VA

CONTENTS

		Page
ABSTRACT		1
INTRODUCTO	N	1
DESCRIPTIO	N OF OUTCROP SECTION	3
DESCRIPTION	ON OF SAMPLE MATERIAL	3
DISCUSSION	l	10
POTENTIAL	ECONOMIC VALUE	13
ACKNOWLEDG	EMENTS	14
	GE	14
REFERENCES	CITED	15
	ILLUSTRATIONS	
Figure 1.	Sirhan-Turayf region, Al Amud work area	2
Figure 2.	Outcrop of the opal claystone	4
Figure 3.	Photomicrographs of siliceous fossils from the opal claystone	5
Figure 4.	X-ray diffraction trace of opal claystone from the Sirhan-Turayf region	6
Figure 5.	Scanning electron microscope image of Rushayda Claystone Bed sample	7
Figure 6.	Scanning electron microscope image of Rushayda Claystone Bed sample silica-rich area	8
Figure 7.	Scanning electron microscope image of a sample from the halite-rich area of the Rushayda Claystone Bed	8
Figure 8.	Location of Sirhan-Turayf region 60 million years ago	11
	TABLE	
Table 1.	Semi-quantitative x-ray emmission analyses of a sample of opal cristobalite rock	9

OPAL CLAYSTONE ASSOCIATED WITH PHOSPHATE ROCK IN NORTHERN SAUDI ARABIA

by

William F. Outerbridge and Charles R. Meissner, Jr.

ABSTRACT

Opal claystone occurs in bedded deposits associated with phosphate rock in the Sirhan-Turayf region of northern Saudi Arabia. A typical sample comprises opal-C (cristobalite) and attapulgite with minor quartz, calcite, and halite. The halite and calcite may be secondary deposits from surface water. Diatom fragments and siliceous sponge spicules suggest that the beds are diagenetically altered diatomite. Deposition may have been on a continental shelf, possibly as an offshore facies of phosphate deposits. Opal-C and attapulgite are co-products of the diagenisis of the diatoms and a clay, possibly montmorillinite.

INTRODUCTION

Opal claystone, a porcelaneous, very low density rock composed of opal cristobalite and clay, similar to that described by Heron and others (1965), was identified in a sample collected from the upper part of the Turayf group of Early Tertiary age (Riddler and others, 1983, 1984) in the Sirhan-Turayf region, in the Al Amud work area south of Turayf. The region has been explored for phosphate rock for several years, beginning with reconnaissance mapping by Mytton (1966) and continuing with detailed studies by Meissner and Ankary (1970). Recent extensive and detailed investigations in the Sirhan-Turayf region by the Riofinex Geological Mission (Kluyver and others, 1981, Riddler and van Eck, 1984), have added greatly to the knowledge of the regional stratigraphy.

In the course of a brief tour by us of the Sirhan-Turayf region (fig. 1), under the auspices of the Riofinex Geological Mission and guided by Clive Aspinall, we found and sampled an opal claystone within the Rushayda claystone bed, above the Arqah phosphorite member, that crops out as a distinct unit in the cyclic sequence of the upper part of the Turayf group (Riddler and others, 1983, 1984). The Turayf group extends from about long 37° 30' E. to long 40° 30' E., and from lat 29°45' N. past lat 32° N. into Jordan and Iraq. An area of more than 100,000 km² in Saudi Arabia has been mapped and parts have been core- and percussion-drilled in the course of phosphate exploration.

1/ U.S. Geological Survey, Reston, VA

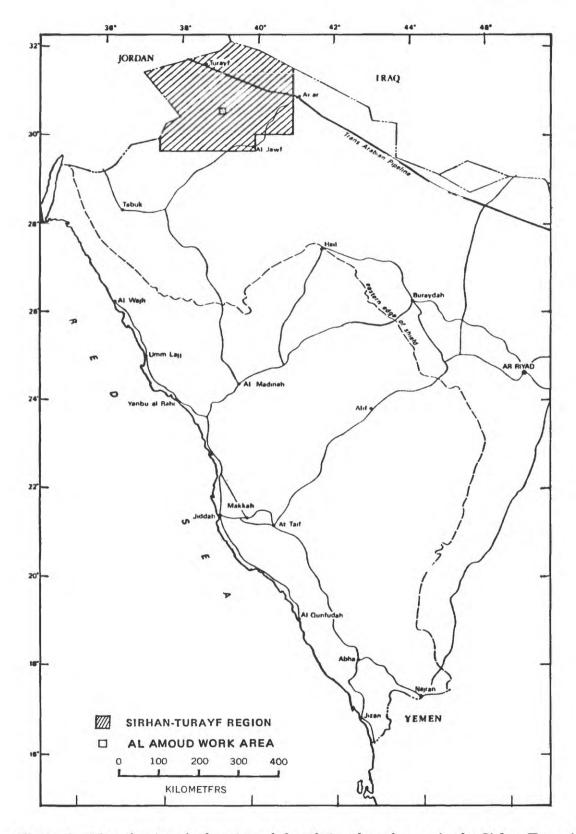


Figure 1.--Map showing the location of the Al Amud work area in the Sirhan-Turayf region.

DESCRIPTION OF THE OUTCROP SECTION

The bed sampled is in the Al Amud member of the Umm Wu'al formation of the Turayf group, which is of Paleocene to Eocene age (fig.2). The Al Amud member lies conformably above the Arqah phosphorite. The opal claystone is part of the Rushayda claystone bed, which is the basal bed of the Al Amud member. The claystone beds consist of a sequence of 1 to 20 cm-thick beds of opal claystone interbedded with calcareous claystone beds of comparable thickness, aggregating about 15 m. The calcareous claystone beds were not sampled. The Rushayda claystone bed is conformably overlain by the Rushayda coquina bed, the upper bed of the Al Amud member. Quaternary-Tertiary basalt lava caps the sedimentary rocks in this area.

DESCRIPTION OF THE SAMPLE MATERIAL

The opal claystone is creamy white (very pale orange 10 YR 9-10/2 (Goddard and others, 1948) with brown (5 YR 4/2) fillings in cracks and light-brown (5 YR 6/4) coatings on exposed surfaces. Under long-wave ultraviolet light the claystone fluoresces deep purplish red. The claystone is porcelaneous, can be scratched with a knife point, breaks with conchoidal fracture, and will ring when two pieces are struck together. It fits the description of porcelanite of Bramlette (1956). When wetted, moisture is quickly absorbed, an indication of its high porosity and permeability. There are no megafossils or obvious internal sedimentary structures. The bulk density is 1.3, half that of quartz.

Microscopic examination by George Andrews (USGS, written commun., 1984), and E.I. Robbins (USGS, written commun., 1984) have determined that most of the original material was degraded beyond recognition, but some silicified sponge spicules, whole and fragmental diatoms, green algae (fig. 3), and silicified foraminifera remain. Ornamentation of the diatom fragments is highly varied, which suggests that many species are represented. One of the diatoms is Early Tertiary in age. In particular, Andrews observed two species of Coscinodiscus, one of Melosira, and a Trinacrea aff. T. conifera (Brightwell) Grunow. This assemblage suggests a marine origin.

Digestion of a portion of the sample in 10% HCL and 48% HF produced an organic residue which amounted to about 0.1 volume-percent of the rock. The residue was predominantly yellow-brown, amorphous remains of organic tissues. Recognizable material in the residue included a charred wood cell, grass cuticle, some degraded sponge spicules, and a degraded sponge plate. Pyrite formed about one percent of the residue. The predominant crystal form was 4 um framboids enmeshed in the tissues. One octahedral pyrite crystal was noted, as well as a rutile twin and two grains of an unidentified pale-blue mineral (E.I. Robbins, written commun., 1984).

X-ray diffraction analysis (Cu K-alpha) showed abundant cristobalite, matching opal-C of Jones and Segnit (1971), with attapulgite, quartz, calcite, and halite (fig. 4).

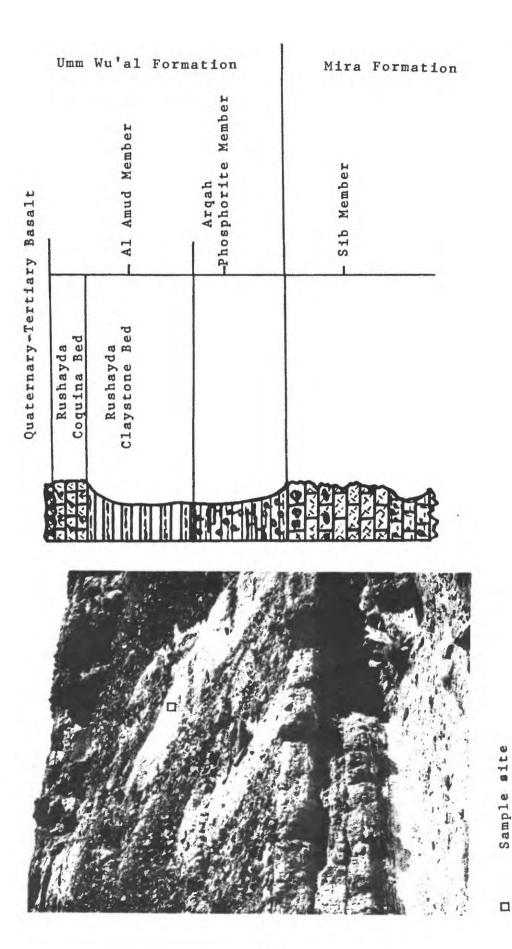


Figure 2 .-- Outcrop of the opal claystone.

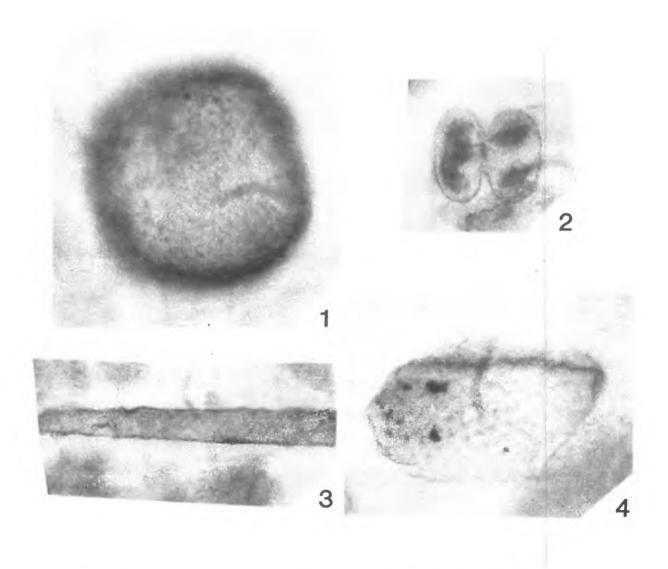


Figure 3.--Photomicrographs of siliceous fossils from the opal claystone

- 1. Coscinodiscus (sp.), an early Tertiary diatom, diameter 60 um.
- 2. A desmid (green alga), 26 um wide.
- 3. Fragment of sponge spicule, 14 x 142 um.
- 4. Probable sponge fragment, 80 um long.

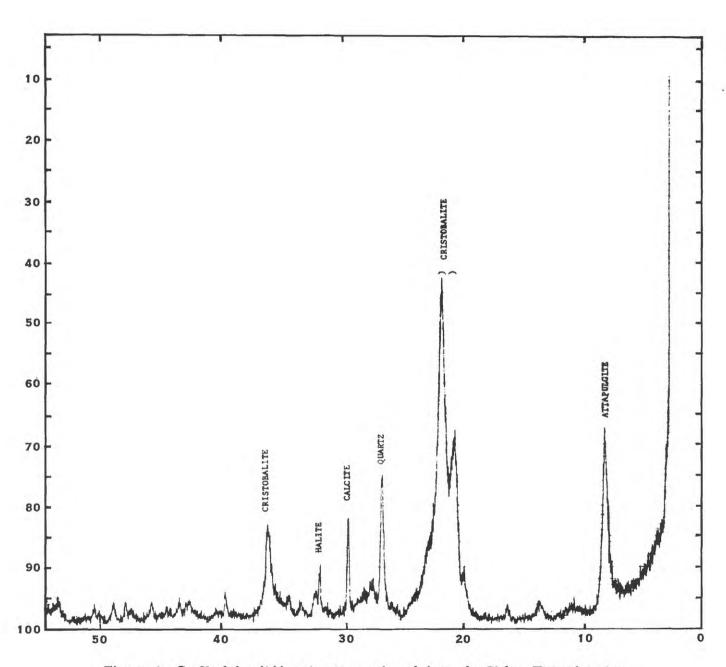


Figure 4.--Cu-K-alpha diffraction trace of opal from the Sirhan-Turayf region.

Scanning electron microscope analysis shows that halite is concentrated in patches surrounded by halite-free areas (fig. 5). Closer examination (fig. 6) shows that the halite-free area has a highly irregular surface of degraded diatoms and fairly well-preserved sponge spicules with molds where spicules and other constituents of the rock have been removed in the breaking of the specimen. A fine fibrous meshwork of attapulgite permeates the specimen. Irregularly shaped, dense white flakes, possibly of calcite, are scattered through the field of the SEM image. A chemical analysis by energy-dispersive x-ray techniques of the area of figure 6 and an estimate of the minerals present based on the analytical results are given in table 1.

The SEM image of the halite-rich area (fig. 7) shows a surface almost entirely covered by halite with feathery overgrowths that may be calcite. Large-scale porosity remains, but the very small-scale porosity of figure 6 is covered, and possibly filled by halite. A chemical analysis by energy-dispersive x-ray techniques of this field and an estimate of the minerals present based on the analytical results are given in table 1. The values for cristobalite, quartz, and attapulgite are most likely from the substrata below the section penetrated by electron beam.

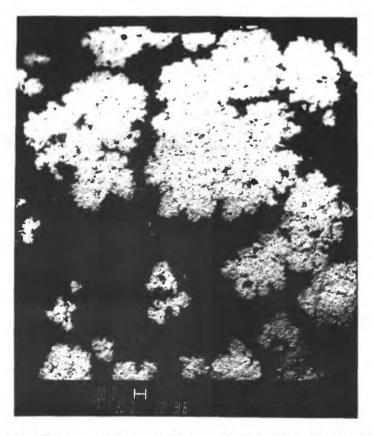


Figure 5.--Scanning electron microscope image of Rushayda claystone bed. Light areas are halite; dark is silica. Bar scale is 100 microns.

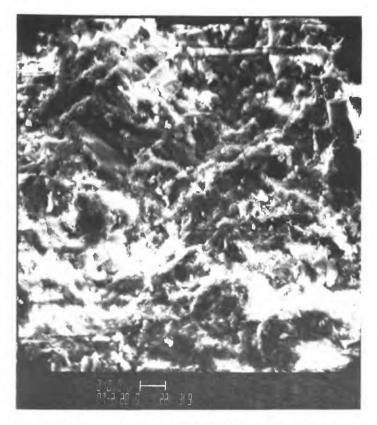


Figure 6.--Scanning electron microscope image of Rushayda claystone bed, silica-rich area. Bar scale is 10 microns.

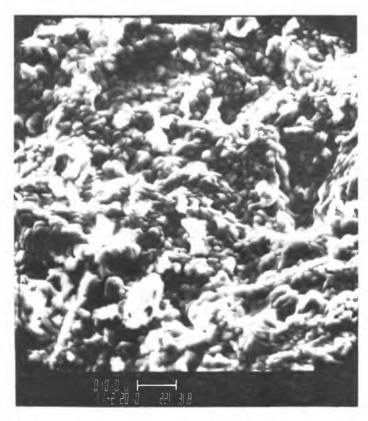


Figure 7.--Scanning electron-microscope image of Rushayda claystone bed, halite-rich area. Bar scale is 10 microns.

Table 1.--Semi-quantitative x-ray emission analyses of a sample of opal cristobalite rock from northern Saudi Arabia.

Weight percent

Element	Silica rich field	Halite rich field
Na	ND	25
Mg	1	LTI
Al	LTI	1
Si	43	16
Cl	LTI	35
K	ND	LTI
Ca	4	1
Fe	LTI	LT1

LT - less than

ND - not detected

X-ray analyzer: EDAX 9100

SEM : ETEC Autoscan

Analysis by Paul Hearn, USGS

DISCUSSION

The opal claystone is an unusual rock and its origin apparently does not fit well with ideas Weaver and Beck (1977) developed in studies of phosphate, attapulgite, and diatom-rich sediments of the southeastern United States. Our hypothesis on the origin of the opal claystone in the Sirhan-Turayf basin is based on detailed examination of the sample, on the largely unpublished stratigraphic interpretation developed during phosphate exploration in the Sirhan-Turayf region, and on current paleogeographic interpretation.

The process of sediment deposition and paleogeographic distribution have been described by Riggs (1984) for the Miocene Atlantic coastal region of the United States, and the position of diatomites in the same units described by Scarborough and others (1980). According to Riggs (1984) and Scarborough and others (1980), whenever the continental shelf is sufficiently covered by water and a condition of oceanic upwelling exists, mud and sand accumulate in drowned stream channels and smaller estuaries, phosphatic sediments accumulate in larger estuaries and on the inner shelf, calcareous sediments accumulate on the middle and outer shelf, and diatomites accumulate at the most seaward part of the sequence. If the water becomes more shallow, the facies shift seaward, and if the water becomes deeper, the facies shift landward.

We believe that a closely analogous situation existed in the Sirhan-Turayf region during the Paleocene and Eocene (Barron and others, 1981, fig. 8). The main differences between the two areas are that the coastline and the main current ran broadly westward here (Haq, 1981, fig. 8) rather than northeastward, and this area lay solidly within the dry band of the northern tropics.

Recognition of diatom remnants supports the interpretation of the opal claystone deposit as a seaward shelf facies of the phosphatic beds, with stratigraphic relations comparable to those of the Pungo River Formation, as described by Scarborough and others (1980). Like the Pungo River Formation, the opal claystone of the Sirhan-Turayf region probably was derived from diatomaceous sediments deposited as a result of diatom blooms associated with upwelling currents and active phosphorite sedimentation. Abundant wood-grained chert in the Turayf group, comparable to that described be DeCelles and Gutschick (1983), reinforces this conclusion.

Bramlette (1956) in his study of the Monterey Formation, California, concluded that diatomites are deposited where nutrients are abundant and detrital sediments are sporadic. In the Monterey Formation, the detritus was trapped before it reached the sites of diatomite deposition by tectonic blocking of streams. The Sirhan-Turayf region is characterized by thin, widespread deposits, which suggest uniform tectonic activity. Detritus was probably transported to the area largely by wind or by ocean current; because the ocean current flowed eastward from the deep sea, the current is viewed as an unlikely sediment vector. This would mean that wind was the primary carrier of the small amount of detritus deposited.

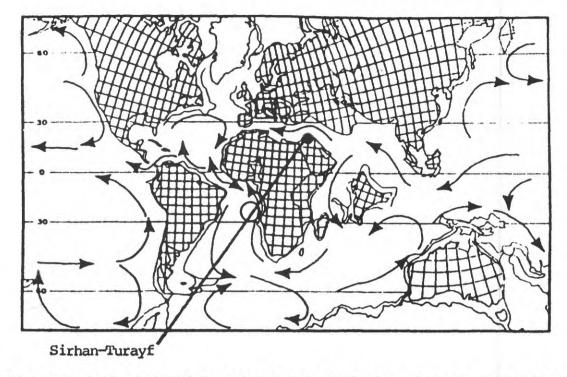


Figure 8.--Location of the Sirhan-Turay fregion 60 Ma ago. Adapted from Barron and others (1981). Estimated ocean surface circulation from Haq (1981).

On the other hand, nutrient-rich water from the deep sea was carried by a westward setting current onto the continental shelf where there is warmth and sunlight in abundance. The nutrient-rich water, warmth and sunlight with the phosphorous and nitrates from the ocean created conditions favorable for extensive blooms of diatoms, which from time to time were the principal source of the opal claystone sediment. Layers of opal claystone in the Rushayda claystone bed represent these times.

The sequence of events began with the accumulation of diatom tests, a probable montmorillonitic clay mineral and sparse foraminifera. The abundance of marine fossils in beds conformably above and below the diatomitic sequence as well as the diatoms strongly suggest that deposition was in a very prolific marine environment.

The occurrence of attapulgite in these sediments leads to a separate problem. Weaver and Beck (1977) state:

"In the southeastern United States primary palygorskite (attapulgite) grew only in environments (bay, lagoon, lake, or soil) where the salinity was less than normal sea water. Palygorskite in marine sediments is either detrital or secondary (by post-depositional circulation of brackish waters). We see no overwhelming reasons to believe this restriction is not universal."

Weaver and Beck (1977) present abundant field evidence as well as evidence from chemical calculations to support their ideas. Their interpretation is commonly accepted in the southeastern United States, and the existence of attapulgite in a sediment with marine fossils is thought to be diagnostic of low salinity water and restricted circulation. But the geographic setting of the Sirhan-Turayf region during Eocene and Paleocene time was such that if a bay or lagoon existed, it would probably be more saline than normal sea water.

In the Sirhan-Turayf region, the opal claystone is underlain and overlain by highly fossiliferous marine limestones and contains diatoms generally considered oceanic or pelagic. No fossils associated with shallow water or restricted circulation have been found. It is likely, on this basis, that the opal claystone is an open water deposit. However, the wood and grass debris recognized in the sample suggests that deposition was not very far from land.

The only clay mineral present in the claystone is attapulgite and for reasons stated below it does not appear that the attapulgite in this deposit is detrital.

The expected path of diagenesis for amorphous silica is opal-A to opal-C to chert to quartz. The rate of the reaction depends on time, temperature, and the geochemical environment of the sediment. The sediments were deposited during Paleocene-Eocene time and the time interval available for diagenesis might be as much as 45 million years for a process that is reported to take a few days to 6 months in the laboratory (Kastner and others, 1977).

Temperature effects on the chemical behavior of silica, magnesia, and pH in sea water in the range from 0 to 60 degrees C. are trivial (Weaver and Beck, 1977); according to Kastner and others (1977) significant factors in the geochemical environment are the concentration of silica in solution, the alkalinity of the solution, the presence of both magnesium and OH⁻, with about twice as much hydroxyl as magnesium, and the presence of reactive clays.

Opal-A transforms to opal-C by a solution-redeposition process which involves a Mg and OH compound as nucleation point for the beginning of crystallization. Opal-C transforms to chert by a solid-state process.

The transformation of opal-A to opal-C is fastest in carbonate sediments, much slower in pure siliceous oozes, and slowest in the presence of reactive clay minerals. The concentration of silica in solution also seems to have an effect on the diagensis of opal-A, with higher concentration favoring the formation of quartz.

Applying Kastner's chemical data and conclusions to the opal claystone layers in the Rushayda claystone bed we find that if we start with diatoms (opal-A) and a reactive clay (preferably montmorillonite) in sea water we can go step by step to the opal-C and attapulgite of the Rushayda claystone bed. Once the sediments reached bottom and came to rest the opal-A began to dissolve and transform to opal-C saturating the water around each diatom with silica.

A small portion of the magnesium and OH settled on the opal-C. By far the larger portion, together with silica, reacted with the clay, forming attapulgite. The process continued until the attapulgite consumed essentially all the magnesium and the alkalinity. The solution of opal-A and deposition of opal-C continued, at a vastly decreased rate, until practically all of the opal-A was consumed. By then the grains had grown together, the ooze had turned to rock, the reactants were depleted, and diagenesis stopped.

In addition to opal-C and attapulgite, the sample contains calcite and halite. Because the entire process happened under salt water and salt did not enter the diagenetic reaction, the rock after diagenesis was saturated with residual salt water. The organic residue and pyrite suggest that at some time during deposition oxygen was depleted. The pale-yellow color of the organic residue suggests that it had never been deeply buried, because organic material darkens on exposure to heat in deep burial. Furthermore, geologic evidence suggests that the beds have been exposed to the weather and circulating ground water since at least Miocene time. It may be that the salt found in the sample is residual from the interstitial sea water and concentrated by crystallization from capillary water at the outcrop. The position of calcite crystals on both the silica and the halite, and the very small amount of calcite in the original material, suggest that the calcite was crystallized from surface water, possibly washed down from the overlying limestone.

Fresh samples collected by drilling from within the deposit should help resolve the problem of whether the salt is original or secondary. This problem is an economic one since salt is considered a corrosive and deleterious substance in some of the uses of this material.

POTENTIAL ECONOMIC VALUE

This opal claystone may be useful as a building stone in the warm, dry region in which it is found, partly because of low bulk density, which reduces the load factor, and partly because of the high porosity, which is associated with good insulation properties. The nearest market for such stone is Taberjal, a new farming town in Wadi Sirhan, about 100 km west of the Al Amud area.

Industrial use of the rock might be in abrasives, refractory insulation, as a filtration medium, and as an absorbant. It would make an excellent absorbent for house-pet waste, and it has a very strong affinity for grease and oil. A potential market for the rock as an industrial raw product is at Yanbu' al Bahr, a major industrial city and port on the Red Sea.

Agricultural use of the rock may be as a moisture-holding agent mixed in irrigated soil of the Sakakah area, about 130 km southeast of the Al Amud area.

ACKNOWLEDGEMENTS

To Gordon Riddler, Marcel van Eck, Clive Aspinall, Anwar Al Farasani, Saleh Dini, and their colleagues of the Riofinex Geological Mission, we express thanks for their hospitality and generous sharing of their knowledge of the geology of northern Saudi Arabia. To Eleanora I. Robbins and George Andrews for isolation and identification of the diatoms and spicules, to Virginia Gonzales and John Hosterman for x-ray analyses, and to Paul Hearn for SEM analyses, and to our other colleagues who rendered aid and comfort as well as good criticism on this paper, the authors give thanks and gratitude.

The work on which this report is based was performed in accordance with the cooperative agreement between the Saudi Arabian Ministry of Petroleum and Mineral Resources and the U.S. Geological Survey.

DATA STORAGE

Data-file USGS-DF-05-04 has been established for the storage of field data and other supporting documents related to this report.

Data on the mineral occurrences in the Sirhan-Turayf region have been updated and entered for the following MODS number:

04260 Al Amud Tripoli New input 12/84

REFERENCES CITED

- Barron, E.J., Harrison, C.G.A., Sloan, J.L., and Hay, W.W., 1981, Paleogeography 180 million years ago to the present; Eclogae Geologicae Helvetiae, v. 74, p. 433-470.
- Bramlette, M.V., 1956, The Monterey Formation of California and the origin of its siliceous rocks: U.S. Geological Survey Professional Paper 212, 57 p.
- DeCelles, P.G., and Gutschick, R.C., 1983, Mississippian wood-grained chert and its significance in the western interior United States: Journal of Sedimentary Petrology, v. 53, no. 4, p. 1175-1191.
- Goddard, E.N., Trask, P.D., De Ford, R.K., Rove, O.N., Singewald, Jr., J.T., and Overbeck, R.M., 1948, Rock-color chart: The Geological Society of America, Boulder, Colorado. Reprinted, 1979, 6 p.
- Haq, B.U., 1981, Paleogene Paleoceanography: Early Cenozoic oceans revisited: Oceanologica Acta, v. 4, p. 71-82.
- Heron, S.D., Jr., Robinson, G.C., and Johnson, Henry, S., 1965, Clays and opal-bearing claystones of the South Carolina coastal plain: State Development Board, Division of Geology, Bulletin No. 31, 66 p.
- Jones, J.B., and Segnit, E.R., 1971, The nature of opal: I. Nomenclature and constituent phases: Journal of the Geological Society of Australia, v. 18, no. 1, p. 57-68.
- Kastner, M., Kastner, J.B., and Gieskes, J.M., 1977, Diagenesis of siliceous oozes--I. Chemical controls on the rate of opal-A to opal-C transformation an experimental study: Geochimica et Cosmochimica Acta, v. 41, p. 1041-1059.
- Kluyver, H.M., Bege, V.B., Smith, G.H., Ryder, J.M., and van Eck, M., 1981, Sirhan-Turayf phosphate project-results of work carried out under the phosphate agreement, 29th Dhual Hijjah 1398-30 Jumad Thani 1401 (29 November 1978-4 May 1981): Saudi Arabian Deputy Ministry for Mineral Resources Technical Record RF-TR-01-05, 77 p., plus appendices.
- Meissner, C.R., Jr., and Ankary, A., 1972, Phosphorite deposits in the Sirhan-Turayf Basin, Kingdom of Saudi Arabia: Saudi Arabian Directorate General of Mineral Resources Mineral Resources Report of Investigations 2, 27 p.
- Mytton, J., 1966, Geologic map of the Turayf phosphate area (with text): Saudi Arabian Directorate General of Mineral Resources Mineral Investigations Map MI-3, scale 1:100,000.
- Riddler, G.P., Khallaf, H.M., Farasani, A.M., 1983, Exploration for phosphate in the Sirhan-Turayf region, northwest Saudi Arabia: Saudi Arabian Deputy Ministry for Mineral Resources Open-file Report RF-OF-03-22, 12 p.
- Riddler, G.P., van Eck, M., Aspinall, N.C., McHugh, J.J., Griffin, M.B., Farasani, A.M., 1984, Lithostratigraphy of the Turayf Group: Open-file RF-OF-04-02, 40 p.

- Riddler, G.P., and van Eck, M., 1984, Sirhan-Turayf phosphate project progress report for 1402-1403 program year (August 1982-August 1983): Saudi Arabian Deputy Ministry for Mineral Resources Open-file Report RF-OF-04-06, 38 p.
- Riggs, S.R., 1984, Paleoceanographic model of Neogene phosphate deposition, U.S. Atlantic Continental Margin: Science, v. 223, No. 4632, p.123-131.
- Scarborough, A.K., Riggs, S.R., and Snyder, Scott W., 1980, Stratigraphy and petrology of the Pungo River Formation, central coastal plain of North Carolina in Scott, T. M., and Upchurch, S.B., 1980, eds. Miocene of the southeastern United States: Florida Bureau of Geology, Special Publication No. 25, p. 49-64.
- Weaver, C.E., and Beck, K.C., 1977, Miocene of the southeastern United States; a model for chemical sedimentation in a perimarine environment: New York, Elsevier Pub., 234 p.